MS analysis: separate analysis of M^+, $M - CO^+$, and $M - 2CO^+$ gave independent measures of deuterium content: **21** *m/e* (int) M^+ 397 (0), 396 (4.1), 395 (25.1), 394 (100), 393 (3.5), 392 (13.4); $M - CO^+$ 369 (0), 368 (3.7), 367 (23.5), 366 (100), 365 (3.7), 364 (13.5); $M - 2CO^+$ 341 (0), 340 4.4), 339 (22.3), 338 (100), 337 (4.0), 336 (13.7). **21** + **21-*d*** *m/e* (int) M^+ 397 (0.0), 396 (31.7), 395 (137.4), 394 (100), 393 (17.3), 392 (12.3) [45.9% **21**, 54.1% **21-*d***]; $M - CO^+$ 369 (4.5), 368 (29.9), 367 (137.0), 366 (100), 365 (17.6), 364 (12.5) [45.5% **21**, 54.5% **21-*d***]; $M - 2CO^+$ 341 (6.3), 340 (30.2), 339 (136.3), 338 (100), 337 (17.5), 336 (12.4) [45.3% **21**, 54.7% **21-*d***]. ^1H NMR analysis (CD_2Cl_2) δ 6.95 (1.00 H, =CH), 4.96 (9.96 H, C_5H_5), 2.80 (0.460 H, CH), 1.25 (6.08 H, CH_3) [46.0% **21**, 54.0% **21-*d***].

Reaction of propene (0.13 atm, 60 mL, 0.33 mmol) with **1** (66 mg, 0.136 mmol) and **1-*d*** (64 mg, 0.132 mmol, 100% d_1) in CH_2Cl_2 (130 mL) at −50 °C for 2 h followed by a $N(CH_3)_3$ (1.0 atm, 235 mL, 10 mmol) qunch gave **15** and **15-*d*** (23 mg, 0.061 mmol, 23%) which were purified by column chromatography and HPLC before analysis.

MS analysis: separate analysis of M^+, $M - CO^+$, and $M - 2CO^+$ gave independent measures of deuterium content: **15** *m/e* (int) M^+ 383 (0), 382 (3.8), 381 (23.5), 380 (100), 379 (3.0), 378 (13.0); $M - CO^+$ 355 (0), 354 (3.8), 353 (22.3), 352 (100), 351 (3.2), 350 (13.3); $M - 2CO^+$ 327 (0), 326 (6.0), 325 (21.5), 324 (100), 323 (3.4), 322 (13.1). **15** + **15-*d*** *m/e* (int) M^+ 383 (4.9), 382 (31.9), 381 (141.5), 380 (100), 379 (18.0), 378 (12.8) [44.8% **15**, 55.2% **15-*d***]; $M - CO^+$ 355 (4.6), 354 (30.3), 353 (142.2), 352 (100), 351 (19.3), 350 (14.0) [44.3% **15**, 55.7% **15-*d***]; $M - 2CO^+$ 327 (0.0), 326 (37.2), 325 (139.0), 324 (100), 323 (18.8), 322 (13.0), [44.8% **15**, 55.2% **15-*d***]. ^1H NMR analysis (CD_2Cl_2) δ 7.08 (1.00 H, =CH), 4.9 (10.00 H, C_5H_5), 2.7 (1.456 H, CH_2 and CHD), 1.17 (3.05 H, CH_3) [45.6% **15**, 54.4% **15-*d***].

(*E*)-1,2-Dideuterio-3,3-dimethyl-1-butene (23-*E*).[31] 3,3-Dimethyl-1-butyne (1.32 atm, 235 mL, 12.8 mmol) was condensed into a solution of $(C_5H_5)_2ZrDCl$ (3.11 g, 12.02 mmol) in toluene (120 mL) at −78 °C. The reaction mixture was stirred at ambient temperature for 2 h. Solvent was evaporated, and the residue was dried under high vacuum for 3 h. Dilute D_2SO_4 (20 mL, 1 M) was added to the residue at −78 °C via syringe. The aqueous solution was stirred for 2 h at ambient temperature. Volatiles were vacuum transferred onto P_2O_5 and then into a storage vessel. **23-E** was isolated as a clear liquid (0.75 atm, 235 mL, 7.3 mmol, 61%) without further purification: ^1H NMR (CD_2Cl_2) δ 4.902 (t, J_{DH} = 2.64 Hz, =CHD), 1.015 (s, $C(CH_3)_3$).

(*Z*)-1,2-Dideuterio-3,3-dimethyl-1-butene (23-*Z*).[31] 1-Deuterio-3,3-dimethyl-1-butene (1.71 atm, 235 mL, 16.6 mmol) was added to a solution of $(C_5H_5)_2ZrDCl$ (3.9 g, 15.1 mmol) in toluene (250 mL) at −78 °C. Workup with H_2SO_4 as described above gave **23-Z** (0.95 atm, 235 mL, 9.2 mmol, 61%) as a clear liquid: ^1H NMR (CD_2Cl_2) δ 4.817 (t, J_{DH} = 1.7 Hz, =CHD), 1.015 (s, $C(CH_3)_3$).

Reaction of 1 with 23-E. **23-E** (0.20 atm, 8 mL, 65 μmol) was condensed into an NMR tube containing a suspension of **1** (13 mg, 27 μmol) in CD_2Cl_2 (0.51 mL) at −78 °C. The NMR tube was sealed under vacuum, warmed to ambient temperature, and centrifuged. Prompt ^1H NMR analysis revealed **10**-threo and **23-E** as the major components: ^1H NMR (CD_2Cl_2) δ 5.36 (s, C_5H_5), 1.95 (br d, J = 11.91 Hz, $\omega_{1/2}$ = 6 Hz, μ-CCHDC*H*D), 1.14 (s, $C(CH_3)_3$).

Reaction of 1 with 23-Z. **23-Z** (0.20 atm, 8 mL, 65 μmol) was condensed into a suspension of **1** (12 mg, 25 μmol) in CD_2Cl_2 (0.42 mL) at −78 °C. Prompt ^1H NMR analysis revealed **10**-erythro and **23-Z** as the major components: ^1H NMR (CD_2Cl_2) δ 5.36 (s, C_5H_5), 1.96 (br s, $\omega_{1/2}$ = 11 Hz, μ-CHDC*H*D), 1.14 (s, $C(CH_3)_3$).

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged. S.R.M. was supported by a fellowship from W. R. Grace. P.J.F. was a National Science Foundation Postdoctoral Fellow. We thank Dr. J. C. Brown and D. F. Snyder for their valuable assistance on the mass spectrum analysis. We are grateful to Professor R. S. Bly for helpful advice and discussion.

Formation of Diiron μ-Alkenyl Complexes from the Reaction of a μ-Methylidyne Complex with Selected Alkenes

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Abstract: Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$, **1**, with 1-methylcyclohexene produced $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC(CH_3)CH_2CH_2CH_2CH_2]^+PF_6^-$, **2**, in 72% yield. (2-Methyl-1-propenyl)benzene and *trans*-stilbene reacted with **1** to give $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC(CH_3)_2(C_6H_5)]^+PF_6^-$, **3**, and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(C_6H_5)_2]^+PF_6^-$, **4**, in 71% and 57% yields. **4** was also obtained from reaction of **1** with 1,1-diphenylethylene in 83% yield. **1** reacted with α-methylstyrene and 2,3,3-trimethyl-1-butene to give $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)(C_6H_5)]^+PF_6^-$, **6**, and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)C(CH_3)_3]^+PF_6^-$, **7**; in 59% and 78% yields. The reaction of **1-d** with 1-methylcyclohexene, 1,1-diphenylethylene, α-methylstyrene, and 2,3,3-trimethyl-1-butene gave the μ-alkenyl complexes with the deuterium label exclusively on the bridging alkenyl carbon. The secondary deuterium kinetic isotope effect for the reaction of 2,3,3-trimethyl-1-butene with **1** was found to be 0.72. The regiochemistry and kinetic isotope effect are consistent with electrophilic addition of **1** to the alkene which produces a carbocation intermediate. Subsequently, this intermediate rearranges by a 1,2-hydrogen or carbon shift to produce the μ-alkenyl product.

The cationic μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$, **1**, forms 1:1 adducts with nucleophiles such as NMe_3 and CO.[1,2] **1** also reacts with alkenes such as ethylene, propene, and isobutylene to add the C–H bond of the methylidyne ligand across the carbon–carbon double bond and to produce new μ-alkylidyne complexes.[3,4] The regiochemistry of this hydrocarbation reaction indicates that the methylidyne carbon acts as an electrophile which adds to the least-substituted carbon of the carbon–carbon double bond.

In the course of examining the scope of the reaction of methylidyne complex **1** with alkenes, we discovered that several

(1) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136.
(2) Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7360–7361.
(3) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.
(4) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173–188.

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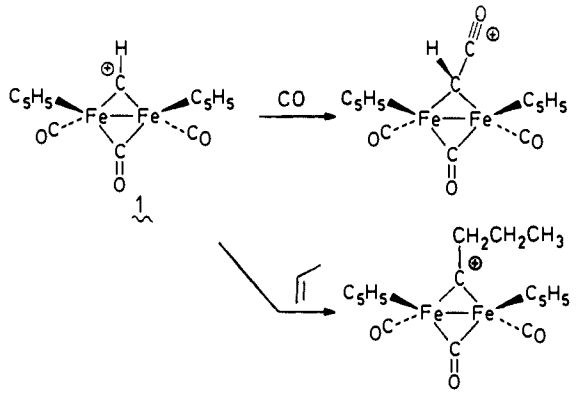
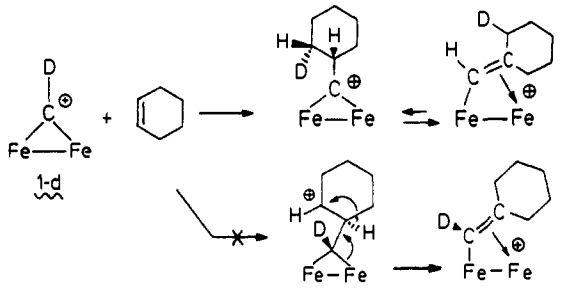


alkenes react with **1** to produce bridging alkenyl complexes rather than bridging alkylidyne complexes.[4] There are two possible pathways for the formation of these bridging alkenyl complexes as detailed below, and we have seen examples of each pathway.[5]

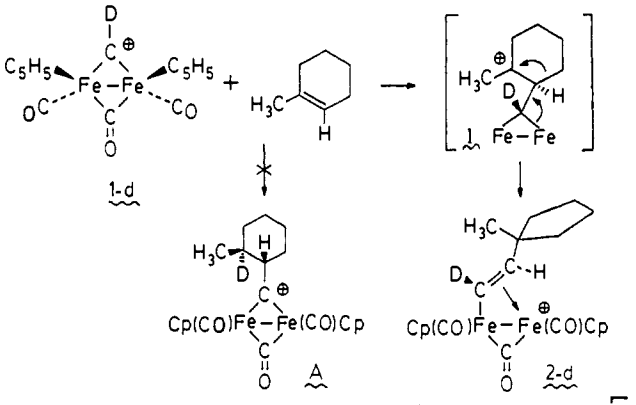
First, the methylidyne complex **1** might add its C–H bond across the carbon–carbon double bond of the alkene to produce a μ-alkylidyne complex that could subsequently rearrange to a μ-alkenyl complex by a 1,2-hydride shift from the α-carbon atom to the bridging carbon atom. The ability of μ-alkylidynediiron complexes to rearrange to μ-alkenyl complexes via 1,2-hydride shifts has been established.[13] In a separate paper, we will present evidence that the μ-alkenyl diiron complexes formed in the reaction of **1** with cyclohexene and 2-butene actually arise by initial formation of a μ-alkylidyne complex followed by rearrangement.[14,15]



The rearrangements of μ-alkylidyne to μ-alkenyl complexes that we have observed have always involved a 1,2-hydrogen shift and never a 1,2-carbon shift. Since some of the μ-alkenyl products formed in the reaction of methylidyne complex **1** with alkenes are the result of carbon migrations, a second pathway for the formation of μ-alkenyl complexes appeared likely. The second direct pathway to μ-alkenyl compounds involves electrophilic addition of the methylidyne carbon to the alkene to generate a carbocation intermediate which then undergoes a 1,2-carbon migration to produce the observed μ-alkenyl product. In this pathway, the C–H bond of the methylidyne ligand is never broken. In this paper, we outline evidence for this electrophilic addition pathway to μ-alkenyl complexes.[3] In addition, we will discuss the factors that determine which alkenes react with **1** to give μ-alkylidyne complexes by a hydrocarbation pathway and which alkenes react with **1** to give μ-alkenyl complexes by an electrophilic pathway.

Results

μ-Alkenyl Complexes Resulting from Carbon Migration. In our first attempt to determine the stereochemistry of hydrocarbation, we studied the reaction of methylidyne complex **1** with 1-methylcyclohexene. If hydrocarbation occurred as anticipated by a cis addition, the axial methine protons in the expected hydrocarbation product **A** would have a large NMR coupling constant. A single product was obtained from **1** and 1-methylcyclohexene, but the appearance of a methyl *singlet* at δ 1.12 conclusively indicated that **A** was not the product. Detailed NMR and IR spectral studies demonstrated that the cationic μ-alkenyl



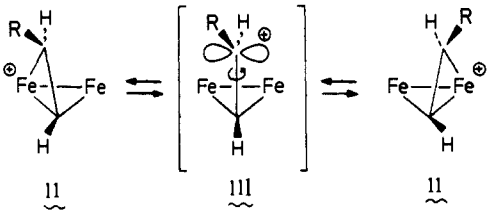
complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC(CH_3)CH_2CH_2CH_2CH_2)^+PF_6^-$, **2**, was formed in 72% isolated yield.

The low-temperature (−70 °C) ^{1}H NMR spectra of **2** in CD_2Cl_2 established the presence of a μ-alkenyl group. The proton on the α-carbon of the bridging alkenyl group appears characteristically[13] far downfield at δ 11.51 as a doublet (J = 12.5 Hz) coupled to the proton on the β-carbon of the μ-alkenyl group which also appears as a doublet at δ 3.55. The methyl group bonded to the quaternary carbon of the cyclopentane ring is responsible for the singlet at δ 1.12. The eight protons on the cyclopentane ring are all nonequivalent and give rise to broad multiplets at δ 1.88 (3 H), 1.73 (3 H), 1.58 (1 H), and 1.46 (1 H). The nonequivalent cyclopentadienyl rings appear as two singlets at δ 5.44 and 5.16.

In the low-temperature (−82 °C) ^{13}C NMR spectra of **2** in acetone-d_6, the α- and β-carbons of the bridging alkenyl group appear at δ 167.4 and 112.1, the nonequivalent cyclopentadienyl rings appear at δ 93.0 and 89.1, the nonequivalent terminal CO ligands appear at δ 215.8 and 209.0, and the bridging CO ligand appears at δ 243.5.

At room temperature, only a single cyclopentadienyl resonance is seen in the ^{1}H NMR at δ 5.33 and in the ^{13}C NMR at δ 90.0. Similarly, only a single resonance for the terminal CO ligands is seen in the ^{13}C NMR at δ 212.3. The coalesence temperature for cyclopentadienyl protons is −42 °C which corresponds to $\Delta G^{\ddagger}$ = 11.0 kcal mol^{-1} for the fluxional process that interconverts the environment of the cyclopentadienyl groups.

Diiron bridging alkenyl compounds can best be viewed as diferrabicyclobutanes (II). In the fluxional process, the α-carbon of the μ-alkenyl compounds remains bonded to both irons while the β-carbon migrates from one iron center to the other. The transition state for the fluxional process (III) has a plane of



symmetry bisecting the iron–iron bond and has a structure similar to that of a cyclopropylcarbinyl cation. The empty p-orbital at the β-carbon of III is stabilized by interaction with the two electron rich C–Fe bonds of the diferracyclopropane ring system. In related studies, we have found that the barrier for the μ-alkenyl fluxional process is decreased by β-alkyl substituents capable of stabilizing the electron deficient β-carbon of transition state III.[13] Previously studied fluxional μ-alkenyl compounds include $[(C_5H_5)(CO)Ru]_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)^+$,[6] $(\mu\text{-}H)Re_2(CO)_8(\mu\text{-}CH{=}CH_2)$,[7]

(5) Numerous other examples of the formation of μ-alkenyls are reported.[6-12]

(6) (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417–1426. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441–442.

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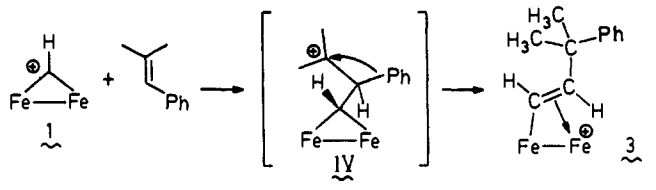
$(C_5H_5)(CO)_5Fe_2(\mu\text{-}CH{=}CH_2)$,[9] and $Os_3(CO)_{10}(\mu\text{-}CH{=}CH_2)$.[11]

The reaction of deuterated methylidyne complex **1-*d*** with 1-methylcyclohexene gave **2-*d*** in which the deuterium label was located on the α-alkenyl carbon atom. This conclusively establishes that deuterium remains bonded to the same carbon throughout the reaction. The site of the label in **2-*d*** was established by the absence of the δ 11.6 resonance in the ^1H NMR spectrum in CD_2Cl_2 and the appearance of a resonance at δ 12 in the ^2H NMR spectrum in acetone. In addition, the doublet at δ 3.77 in **2** collapsed to a singlet in **2-*d*** upon deuterium replacement of the coupled α-alkenyl hydrogen.

The formation of **2** is best explained by initial electrophilic addition of the methylidyne carbon of **1** to the less-substituted end of the carbon–carbon double bond of 1-methylcyclohexene which produces the tertiary carbocation intermediate I. Exclusive *carbon migration* to the cationic center accomplishes the requisite ring contraction. This carbon migration is accompanied by electron donation from an iron–carbon bond and leads directly to the μ-alkenyl complex.

The reaction of **1** with (2-methyl-1-propenyl)benzene gave the μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC(CH_3)_2C_6H_5)^+PF_6^-$, **3**, in 71% isolated yield. In the ^1H NMR of **3**, the trans vinyl hydrogens give rise to two doublets (J = 12.5 Hz) at δ 11.96 and 3.83. At room temperature the fluxional process that interconverts the two enantiomers of **3** is fast on the NMR time scale, the two diastereotopic cyclopentadienyl groups of **3** give rise to a singlet at δ 5.56, and the two diastereotopic allylic methyl groups give rise to a singlet at δ 1.75.

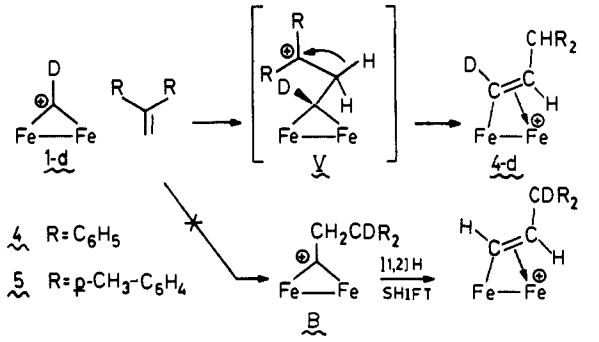


The formation of **3** is best explained by electrophilic addition of the methylidyne carbon of **1** to the phenyl-substituted end of the carbon–carbon double bond of (2-methyl-1-propenyl)benzene which generates the tertiary carbocation intermediate IV. Exclusive phenyl migration to the tertiary carbonium ion center leads directly to μ-alkenyl product **3**.

In the reaction of **1** with *trans*-stilbene, a similar phenyl migration occurred to produce the μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(C_6H_5)_2]^+PF_6^-$, **4**, in 57% yield. In the formation of **2**, **3**, and **4**, where a μ-alkenyl complex could have been produced by either a carbon or a hydrogen migration within an intermediate carbocation, only the μ-alkenyl product of carbon migration was observed.

μ-Alkenyl Complexes Resulting from Hydrogen Migration. The reaction of **1** with 1,1-diphenylethylene produces an 83% yield of the same μ-alkenyl complex **4** that was obtained from *trans*-stilbene. In this case, however, the product arises from a net hydrogen migration instead of a phenyl migration.

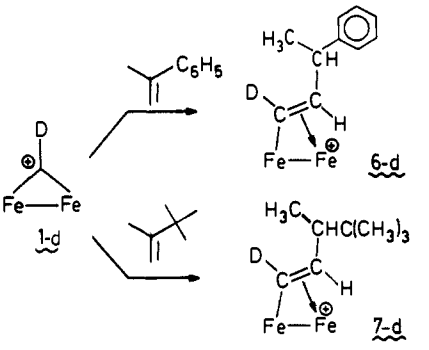
There are two possible mechanisms for this net 1,2-hydrogen migration that are readily distinguished by deuterium labeling studies using **1-*d***. First, addition of the methylidyne carbon **1-*d*** to the methylene unit of 1,1-diphenylethylene would produce the diphenylcarbocation V. A subsequent 1,2-hydride shift would produce **4-*d*** with the deuterium label on the bridging carbon of the μ-alkenyl group. The alternative mechanism would involve addition of the C–D bond of **1-*d*** across the carbon–carbon double bond of diphenylethylene to produce cationic μ-alkylidyne complex **B** which could subsequently rearrange to μ-alkenyl complex **4** by a 1,2-hydrogen shift. This later mechanism would produce **4** with



deuterium label at the benzylic position. Reaction of **1-*d*** with 1,1-diphenylethylene gave **4-*d*** in which the deuterium label was located exclusively on the bridging carbon of the μ-alkenyl group. In the $^2H\{^1H\}$ NMR of **4-*d***, the only resonance observed was a singlet at δ 12.4. This experiment clearly demonstrates that the C–D bond remains intact throughout the reaction.

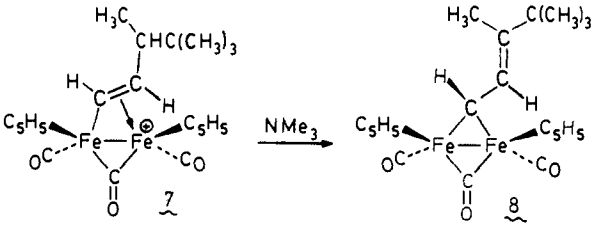
Similarly, reaction of 1,1-di-*p*-tolylethylene with **1** gave μ-alkenyl complex **5** in 72% yield.

The reaction of **1** with α-methylstyrene and with 2,3,3-trimethyl-1-butene also led to formation of μ-alkenyl complexes by way of initial carbocation formation followed by a 1,2-hydrogen shift. The μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)(C_6H_5)]^+PF_6^-$, **6**, was obtained in 59% yield from **1** and α-methylstyrene. Reaction of **1-*d*** with α-methylstyrene gave **6-*d*** with the deuterium label located exclusively at the bridging carbon of the μ-alkenyl complex. Similarly, reaction of **1** and 2,3,3-trimethyl-1-butene gave the μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)C(CH_3)_3]^+PF_6^-$, **7**, in 78% yield, and **1-*d*** gave **7-*d*** with all the deuterium label located at the bridging carbon of the μ-alkenyl group.



In all these cases where hydrogen migration in a carbocation intermediate led to formation of a μ-alkenyl group, hydrogen was the only group available to migrate.

Deprotonation of μ-Alkenyl Complexes to Vinyl Carbene Complexes. Reaction of μ-alkenyl complex **7** with trimethylamine in dichloromethane led to deprotonation and formation of the bridging vinyl carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH{=}C(CH_3)C(CH_3)_3]$, **8**, in 60% isolated yield. Two isomers of **8** which differ in the configuration of the uncomplexed alkene unit were observed in a 12:1 ratio. In the ^1H NMR of **8**, the resonance due to the proton bonded to the bridging carbene carbon appears at δ 12.3 as a doublet (J = 13 Hz) coupled to the vinyl hydrogen at δ 6.8. The large magnitude of this coupling constant suggests a dihedral angle of nearly 180° for this sp^3 CH–CH sp^2



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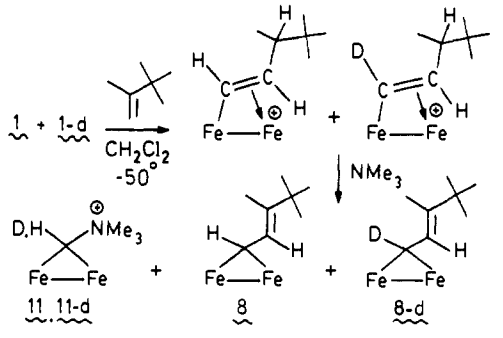
system.[16] Only one cyclopentadienyl resonance is seen at δ 4.86 in the ^1H NMR and at δ 87.1 in the ^{13}C NMR which indicates that the cyclopentadienyl groups are in a cis configuration.

Previously, we have observed addition of nucleophiles such as hydride from $HFe(CO)_4^-$ and hydroxide from aqueous bicarbonate solutions to the β-carbon of cationic bridging alkenyldiiron complexes.[13] However, we have seen no evidence for nucleophilic addition of NMe_3 to μ-alkenyl complex **7**. When **7** was stirred with aqueous bicarbonate, both deprotonation to give **8** and nucleophilic addition of hydroxide to **7** were observed.

Deprotonation of the benzylic hydrogen of μ-alkenyl complex **4** and **6** to vinyl carbene complexes can be accomplished with either aqueous bicarbonate or with trimethylamine. Treatment of μ-alkenyl complex **4** derived from **1** and 1,1-diphenylethylene with aqueous bicarbonate and acetone led to the isolation of the vinyl carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH{=}C(C_6H_5)_2]$, **9**, in 46% yield from **1**. Similarly, deprotonation of **6** with aqueous bicarbonate gave a 44% yield of a 7:3 mixture of the *E* and *Z* isomers about the carbon–carbon double bond of the vinyl carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}C(CH_3)C_6H_5)$, **10-Z** and **10-E**. The major isomer was assigned the *E* configuration on the basis of the farther downfield ^1H NMR chemical shift of the vinyl hydrogen cis to the phenyl group in **10-E** (δ > 7.2) compared with that trans to the phenyl group in **10-Z** (δ 6.86).[17] The hydrogens on the bridging carbene carbon appear as doublets at δ 12.2 for **10-E** and 11.6 for **10-Z**.

Kinetic Isotope Effect on μ-Alkenyl Formation. Labeling studies using **1-*d*** and 2,3,3-trimethyl-1-butene gave μ-alkenyl complex **7-*d*** with the deuterium label exclusively on the bridging carbon. This indicates that the C–D bond is never broken during the reaction.

The secondary deuterium kinetic isotope effect was measured for the reaction of a tenfold excess of 2,3,3-trimethyl-1-butene with a 1.0:1.0 ratio of **1**:**1-*d*** at −50 °C by using a competition technique.[18] The reaction was quenched after 26% consumption of methylidyne complexes by the addition of trimethylamine. Trimethylamine reacts immediately with the unreacted μ-methylidyne complexes to give the amine addition products **11** and **11-*d***.[4] The amine also deprotonates μ-alkenyl complexes **7** and **7-*d*** to give the bridging vinyl carbene complexes **8** and **8-*d***.



The relative amounts of **8** and **8-*d*** were determined by slowly scanning the M^+ and the $M - CO^+$ envelopes in the mass spectrum and averaging 20 scans. The ratio of **8**:**8-*d*** was found to be 45.0:55.0 by using the M^+ envelope and 44.8:55.2 by using the $M - CO^+$ envelope. The isotope effect was calculated to be 0.72 by using M^+ data and 0.71 by using $M - CO^+$ data and the equation $k_H/k_D = [\ln([\mathbf{1}]_t/[\mathbf{1}]_0)]/[\ln([\mathbf{1\text{-}d}]_t/[\mathbf{1\text{-}d}]_0)]$.[18] In four independent experiments, the value of k_H/k_D varied over the range 0.69–0.76.

The ratio of **8**:**8-*d*** was independently confirmed by ^1H NMR. Comparison of the integral for the bridging carbene hydrogen at δ 12.3 to the integral for the vinyl hydrogen at δ 6.8 indicated a ratio of **8**:**8-*d*** of 42.9:57.1. In four experiments, the value of the isotope effect determined by ^1H NMR integration varied from 0.66 to 0.73.

Discussion

In the preceding paper, we described the reactions of methylidyne complex **1** with ethylene, monosubstituted alkenes, and isobutylene that involved a net 1,2-addition of the methylidyne C–H bond across the carbon–carbon double bond and that produced μ-alkylidyne complexes.[18] In contrast, in this paper we describe reactions of **1** with more highly substituted alkenes that lead to μ-alkenyl complexes. Here we will first discuss the mechanism for the formation of μ-alkenyl complexes and then outline the factors which control whether μ-alkylidyne or μ-alkenyl compounds will be produced in the reaction of **1** with a given alkene.

The regiochemistry of the reaction of **1** with α-methylstyrene, 1,1-diphenylethylene, 1-methylcyclohexene, and 2,3,3-trimethyl-1-butene involves clean addition of the methylidyne carbon to the less-substituted carbon of the double bond. This regiochemistry provides evidence for the development of positive charge at the more-substiuted carbon of the double bond at the transition state. For (2-methyl-1-propenyl)benzene, addition of **1** to the less-substituted carbon of the alkene occurred. In this case, the resulting tertiary carbocation is approximately as stable as the alternative secondary benzylic carbocation;[19] therefore, the observed regioselectivity is probably the result of attack of the less-crowded terminus of the double bond.

The regiochemistry of the hydrocarbation reaction in which **1** reacts with alkenes to give μ-alkylidyne complexes is the same as that seen here for μ-alkenyl formation. This suggests that the transition states for both reactions involve extensive carbon–carbon bond formation and development of positive charge at the more-substituted end of the alkene.

The moderately large inverse secondary deuterium isotope effect (k_H/k_D = 0.7 at −50 °C) observed in the reaction of **1-*d*** with 2,3,3-trimethyl-1-butene is best explained by a change in hybridization of the methylidyne C–H bond during the reaction. The C–H bond of **1** is nominally sp^2 hybridized; this is supported by the large value for the ^{13}C–^1H NMR coupling constant of 170.5 Hz.[20] The transition state should have a hybridization closer to sp^3. Models for the transition state are the bridging CH_2 complex which has a ^{13}C–^1H NMR coupling constant of 145 Hz and the bridging alkenyl complex **2** (which can also be viewed as a diiron bicyclobutane) which has a ^{13}C–^1H coupling constant of 154 Hz for the hydrogen attached to the carbon bridge. The inverse isotope effects seen in reactions where a C–H bond changes from sp^2 to sp^3 hybridization is attributed to a stiffening of C–H bending vibrations.[21-23] Examples of inverse kinetic deuterium isotope effects for reactions involving an sp^2–sp^3 change in hybridization include 0.84 for the cycloaddition of a ketene to a deuterated cyclopentadiene[24] and 0.94 for the cycloaddition of ozone to ethylene.[25]

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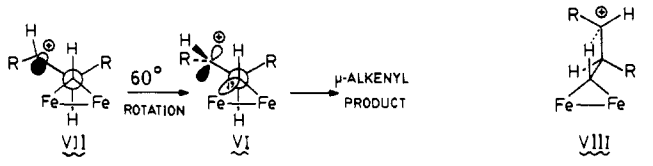
The inverse isotope effect seen for μ-alkenyl formation was not unexpected since the C–D bond is maintained throughout the reaction. The similar inverse isotope effects (k_H/k_D = 0.72–0.81) reported in the preceding paper[18] for hydrocarbation reactions in which the C–D bond is broken during the production of μ-alkylidyne complexes were initially surprising. The inverse secondary isotope effects seen for μ-alkenyl and μ-alkylidyne formation again suggest similar transition states for both reactions that are dominated by carbon–carbon bond formation.

The initial carbon–carbon bond formation in the reaction of **1** with an alkene generates a carbocation intermediate. In the case of μ-alkenyl formation, further evidence for the carbocation intermediate is provided by the observed 1,2-carbon or hydrogen migrations to the cationic center. The μ-alkenyl products formed by a net 1,2-hydrogen shift could have been formed either by initial formation of a μ-alkylidyne complex that subsequently rearranged to a μ-alkenyl complex or by electrophilic addition of **1** to the alkene followed by a 1,2-hydride shift to the carbocation center. For the reactions of 1,1-diphenylethylene, α-methylstyrene, and 2,3,3-trimethylethylene reported here, deuterium labeling studies require the electrophilic addition–1,2-hydride shift mechanism. In a subsequent paper, we will describe reactions of **1** with 2-butene and cyclohexene where μ-alkenyl products arise from the alternate mechanism of μ-alkylidyne formation and subsequent rearrangement.[14,15] In cases where either carbon or hydrogen migration would have given a μ-alkenyl complex, only the product of carbon migration was observed.

The transition states for the reaction of **1** with alkenes that lead to μ-alkylidyne or to μ-alkenyl complexes are very similar and involve only C–C bond formation to give a carbocation intermediate. The two different types of products are the result of a 1,3-hydride shift to the carbocation center that produces a μ-alkylidyne complex and of a 1,2-hydride or carbon shift that produces a μ-alkenyl complex. Quite different conformations of the carbocation intermediate are required for μ-alkenyl and μ-alkylidyne formation as outlined below. Because the conformations required for the 1,2- and 1,3-hydride shifts are so different, their relative energies will depend strongly on steric interactions within each product-forming transition state.

We propose that the geometry of the transition state leading from the carbocation intermediate to the μ-alkenyl product is similar to that of VI. In this conformation, the empty p-orbital at the carbocation center and the bond from carbon to the migrating group are nearly parallel which should facilitate the migration. In addition, the bond from carbon to the migrating group is nearly antiperiplanar to a carbon–iron σ bond. In this geometry, donation of electrons from iron to the carbon bearing the migrating group can provide anchimeric assistance to the migration process by forming the new iron–carbon bond present in the μ-alkenyl product. It should be noted for VI that the dihedral angle between the C–H bond derived from the methylidyne group and C–C bond derived from the alkene is about 60°.

In going from an alkene to VI, the former carbon–carbon double bond has twisted greatly. We think of this as occurring in two stages. First, carbon–carbon bond formation from the methylidyne carbon of **1** to one end of the alkene causes a change in hybridization at the alkene carbon from sp^2 to sp^3 in the carbocation intermediate VII; this increases the dihedral angle between substituents on the former double bond from 0 to 30°. Next an additional 60° rotation about the former double bond aligns the empty p-orbital and a potential migrating group as shown in VI.



VII VI VIII

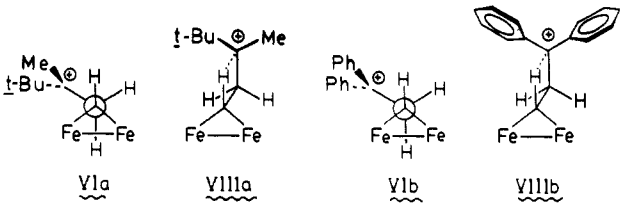
Nothing is known about the relative orientation of the methylidyne C–H bond and the carbon–carbon double bond during initial carbon–carbon bond formation. However, we believe that the orientation of the immediate precursor of μ-alkenyl products must be very similar to VI. In VI, the second substituent attached to the carbon bearing the migrating group is directed toward the highly congested diiron portion of the intermediate. The preference for carbon migration over hydrogen migration is probably a result of the ability of the small hydrogen substituent to occupy this crowded site. The preference for carbon migration is not the result of the inability of hydrogen to migrate since hydrogen migration was seen in the reactions of 1,1-diphenylethylene, α-methylstyrene, and 2,3,3-trimethyl-1-butene.

The geometry of the transition state leading from the carbocation intermediate to the μ-alkylidyne product is similar to that shown for VIII. In this conformation, the dihedral angle between the carbon hydrogen bond derived from the methylidyne ligand and the former carbon–carbon double bond of the alkene is 0°. The empty p-orbital of the carbocation also lies in the plane of these two bonds. This geometry allows a smooth 1,3-hydride shift to generate the μ-alkylidyne product. This transition state is very similar to an edge-protonated cyclopropane. In VIII, there is a moderate steric repulsion between substituents on the carbon bonded to the former methylidyne carbon and the sterically congested iron centers. In addition, large substituents at the carbocation center in VIII may make it difficult to bring the C–H bond close enough for a facile 1,3-hydride shift to occur.

The basic difference between VI and VIII is that in VIII the C—H and C═C bonds are aligned while in VI they are twisted 60° out of alignment. We will now discuss how steric interaction of substituents within VI and VIII determine whether a given alkene will react to form a μ-alkenyl or μ-alkylidyne product.

For the reactions of ethylene, most monosubstituted alkenes, and isobutylene, there are no major steric interactions which would affect the energies of the product-determining transition states VI and VIII. In these cases, only μ-alkylidyne products were observed. This indicates that, in the absence of special steric interactions, transition state VIII for a 1,3-hydride shift of the intermediate carbocation is preferred.

For 2,3,3-trimethyl-1-butene, transition state VIIIa has an unfavorable interaction between the *tert*-butyl group and the iron complex. This interaction is not present in VIa where the *tert*-butyl group has been turned away from the iron center. The tendency of a *tert*-butyl group to destabilize VIII vs. VI is not an overriding effect since transition state VIII leading to a μ-alkylidyne complex is favored for *tert*-butylethylene. Transition state VIIIa may also be destabilized by the bulky substituents at the carbocation center that makes a 1,3-hydride shift difficult. This steric effect would be larger for the methyl and *tert*-butyl substituents present in VIIIa than for the comparable transition state derived from *tert*-butylethylene.

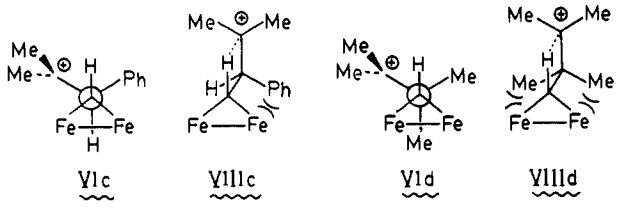


VIa VIIIa VIb VIIIb

For 1,1-diphenylethylene, transition state VIIIb has unfavorable steric interaction with the iron center due to the expected propeller like conformation of the phenyl groups in the carbocation intermediate. This interaction is partially relieved in VIb. Alternatively, the bulky substituents on the carbocation center of VIIIb may make a 1,3-hydride migration quite difficult. In contrast, the relationship between the carbocation center and the C–H bond that undergoes a 1,2-migration to give μ-alkenyl product **4** is unaffected by the steric bulk of the carbocation center.

For 1-methylcyclohexene, (2-methyl-1-propenyl)benzene, and *trans*-stilbene, the carbocations formed by addition of **1** all have *one* carbon substituent on the carbon bonded to the former methylidyne carbon. In the transition state VIIIc leading to an alkylidyne complex, there is apparently a substantial steric repulsion between this carbon substituent and one of the iron centers. This steric repulsion is relieved when the substituent is turned away

from iron in transition state VIc. It should be noted again that only a sterically small hydrogen is directed toward the iron centers in VIc. Thus, the alkyl group of VIc is antiperiplanar to a carbon–iron bond and set up for migration to give a μ-alkenyl product.



VIc VIIIc VId VIIId

For tetramethylethylene[18] and 4-(trimethylsilyl)-2-methyl-2-butene,[26] the carbocations formed by addition of **1** have *two* methyl groups atttached to the carbon bonded to the former methylidyne carbon. The transition state for alkyidyne formation VIIId is destabilized by interaction of these two methyl groups with the two iron centers and by interaction of the tertiary carbocation center with the C–H bond of the former methylidyne group. Nevertheless, VIIId is more stable than the alternate transition state VId for μ-alkenyl formation. In VId, a methyl group is directed toward the very crowded diiron group. This single interaction is large enough to disfavor μ-alkenyl formation.

We first observed μ-alkenyl complexes in the reactions of highly substituted alkenes with **1** and noted an empirical correlation between μ-alkenyl formation and the ability to form an electronically stabilized tertiary or benzylic carbocation intermediate. However, the ability to form such a stabilized carbocation intermediate is not a sufficient condition for μ-alkenyl formation since isobutylene which could form a tertiary carbocation intermediate and styrene which could form a benzylic carbocation intermediate both reacted with **1** to produce μ-alkylidyne products.[18] Apparently the steric effects outlined above are more crucial in determining the nature of the products obtained from **1** and a given alkene. Nevertheless, the observation that cyclopropylethylene[27] is the only monosubstituted alkene to give a μ-alkenyl product and the known high stability of cyclopropylcarbinyl cations suggest that transition state VI for μ-alkenyl formation may be more sensitive to electronic effects than transition state VIII for μ-alkylidyne formation.

The regiochemistry of the reaction of **1** with alkenes to form either μ-alkylidyne or μ-alkenyl products strongly support the formation of a carbocation in the transition state. The relative rates[18] of μ-alkylidyne formation from ethylene (1), propene (56), and isobutylene (6900) also indicate that the developing carbocation is stabilized by electron-donating alkyl groups. Styrene reacts with **1** to form a μ-alkylidyne product about twice as fast (160:90) as 1,1-diphenylethylene reacts with **1** to form a μ-alkenyl product. Apparently, the steric bulk of the two phenyl groups of 1,1-diphenylethylene more than offsets the electronic stabilization of a second electron-donating phenyl group.

Experimental Section

General Methods. See preceeding paper.[18]

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC(CH_3)CH_2CH_2CH_2CH_2)^+PF_6^-$, (2). 1-Methylcyclohexene (0.60 mL, 49 mg, 0.51 mmol) was condensed into a stirred solution of **1** (122 mg, 0.252 mmol) in CH_2Cl_2 (5 mL) at −78 °C, and then the reaction mixture was warmed to ambient temperature. After 45 min, solvent was removed under vacuum, and the resulting solid was dissolved in acetone (2 mL) and filtered. Addition of diethyl ether (10 mL) produced an olive-brown precipitate which was washed with ether (2 × 1 mL) and dried under vacuum to give pure **2** (106 mg, 72%): ^{1}H NMR (CD_2Cl_2, 30 °C) δ 11.59 (d, J = 12.5 Hz, FeC*H*=CH), 5.33 (s, 10 H, C_5H_5), 3.68 (d, J = 12.5 Hz, FeCH=C*H*), 1.88 (br m, 6 H, cyclopentyl), 1.62 (br m, 2 H, cyclopentyl), 1.24 (s, CH_3); ^{1}H NMR (CD_2Cl_2, −70 °C) δ 11.51 (d, J = 12.5 Hz, FeC*H*=CH), 5.44 (s, 5 H, C_5H_5), 5.16 (s, 5 H, C_5H_5), 3.55 (d, J = 12.5 Hz, FeCH=C*H*), 1.88 (br m, 3 H, cyclopentyl), 1.73 (br m, 3 H, cyclopentyl), 1.58 (br m, 1 H, cyclopentyl), 1.46 (br m, 1 H, cyclopentyl), 1.12 (s, CH_3); ^{13}C{^{1}H} NMR (acetone-d_6, 0 °C) δ 242.0 (μ-CO), 212.3 (CO), 166.3 (Fe*C*H=CH, J_{CH} = 154 Hz from gated decoupled spectrum), 114.3 (FeCH=*C*H, J_{CH} = 147 Hz from gated decoupled spectrum), 90.8 (C_5H_5), 51.0 (*C*CH$_3$), 41.0 (CH_2), 27.2 (CH_3), 25.8 (CH_2); ^{13}C{^{1}H} NMR (acetone-d_6, −82 °C) δ 243.5 (μ-CO), 215.8 (CO), 209.0 (CO), 167.4 (Fe*C*H=CH, 112.1 (FeCH=*C*H), 93.0 (C_5H_5), 89.1 (C_5H_5), 50.8 (*C*CH$_3$), 44.0 (CH_2), 36.0 (CH_2), 27.5 (CH_3), 26.2 (CH_2), 25.4 (CH_2); IR (CH_2Cl_2) 2027 (s), 2002 (m), 1868 (m) cm^{-1}. Coalescence of the Cp proton resonances of **2** occurs at −42 °C, τ_c = 5.99 × 10^{-3} s; $\Delta G^{\ddagger}$ (−42 °C) = 11.0 kcal mol^{-1}. Anal. Calcd for $C_{21}H_{23}F_6Fe_2O_3P$: C, 43.48; H, 4.00; P, 5.34. Found: C, 43.35; H, 3.84; P, 5.22.

Similarly, reaction of **1-*d*** (125 mg, 0.258 mmol) with 1-methylcyclohexene (0.58 mmol) gave **2-*d*** (130 mg, 87%): ^{2}H{^{1}H} NMR (acetone) δ 12.07 (s).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC(CH_3)_2C_6H_5)^+PF_6^-$, (3). (2-Methyl-1-propenyl)benzene (65 μL, 60 mg, 0.45 mmol) was added to **1** (165 mg, 0.341 mmol) in CH_2Cl_2 (45 mL) at −78 °C. Recrystallization from acetone–ether gave brown-red **3** (150 mg, 71%): ^{1}H NMR (acetone-d_6) δ 11.96 (d, J = 12.5 Hz, μ-CH), 7.7–7.3 (m, C_6H_5), 5.56 (s, 10 H, C_5H_5), 3.83 (d, J = 12.5 Hz, =CH), 1.75 (s, 6 H, CH_3); ^{13}C{^{1}H} NMR (CD_3NO_2) δ 239.5 (μ-CO), 212.8 (CO), 165.9 (μ-CH), 146.9, 129.8, 128.0, 127.7 (C_6H_5), 114.7 (=CHR), 90.6 (C_5H_5), 46.5 (CMe_2Ph), 29.4 (CH_3); IR (KBr) 2017 (s), 1997 (sh), 1862 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{23}F_6Fe_2O_3P$: C, 46.79; H, 3.76. Found: C, 46.76; H, 3.68.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(C_6H_5)_2)^+PF_6^-$ (4). CH_2Cl_2 (8 mL) was condensed into a flask containing **1** (136 mg, 0.281 mmol) and *trans*-stilbene (60 mg, 0.33 mmol) at −78 °C. Solvent was removed under vacuum at ambient temperature, and the resulting solid was dissolved in acetone (5 mL) and filtered. The solution was concentrated to 1 mL, and diethyl ether (5 mL) was added to precipitate crystalline **4** (106 mg, 57%).

Addition of 1,1-diphenylethylene (30 μL, 0.17 mmol) to **1** (60 mg, 0.124 mmol) in CH_2Cl_2 at −78 °C also led to the isolation of **4** (166 mg, 83%): ^{1}H NMR (acetone-d_6) δ 12.39 (d, J = 12.2 Hz, μ-CH), 7.7–7.3 (m, 10 H, C_6H_5), 5.58 (s, 10 H, C_5H_5), 4.93 (d, J = 10.2 Hz, $CHPh_2$), 4.34 (dd, J = 12.2, 10.2 Hz, =CHR); ^{13}C{^{1}H} (acetone-d_6, −70 °C) δ 242.2 (μ-CO); 214.4 (CO), 177.5 (μ-CH), 145.2, 142.6, 129.5, 128.6, 128.1, 127.7 (C_6H_5), 96.6 (=CHR), 93.0, 89.3 (C_5H_5), 62.5 (CPh_2); IR (CH_2Cl_2) 2031 (s), 2003 (m), 1860 (m) cm^{-1}. Anal. Calcd for $C_{28}H_{23}F_6Fe_2O_3P$: C, 50.64; H, 3.49. Found: C, 50.77; H, 3.84.

Similarly, reaction of **1-*d*** (95 mg, 0.196 mmol) with 1,1-diphenylethylene (50 μL, 0.28 mmol) in CH_2Cl_2 at ambient temperature gave **4-*d*** (25 mg, 20%): ^{2}H{^{1}H} NMR (acetone) δ 12.45.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(C_6H_4\text{-}p\text{-}CH_3)_2)^+PF_6^-$ (5). A solution of 1,1-di-*p*-tolylethylene (300 mg, 1.44 mmol) and **1** (520 mg, 1.07 mmol) in CH_2Cl_2 (45 mL) was warmed from −78 °C to ambient temperature. Recrystallization from acetone–ether gave **5** (530 mg, 72%): ^{1}H NMR (acetone-d_6) δ 12.36 (br d, μ-CH), 7.45 (d, J = 8 Hz, 4 H, C_6H_4), 7.21 (d, J = 8 Hz, 4 H, C_6H_4), 5.55 (s, 10 H, C_5H_5), 4.83 (d, J = 10.2 Hz, $CHAr_2$), 4.32 (br t, =CHR), 2.32 (s, 6 H, CH_3); ^{13}C{^{1}H} NMR (acetone-d_6) δ 212.2 (CO), 176.3 (μ-CH=), 141.0, 137.2, 130.2, 128.4 (C_6H_4), 99.1 (=CHR), 91.0 (C_5H_5), 61.9 ($CHAr_2$), 20.8 (CH_3); IR (CH_2Cl_2) 2033 (s), 2002 (w), 1863 (m) cm^{-1}. Anal. Calcd for $C_{30}H_{27}F_6Fe_2O_3P$: C, 52.06; H, 3.93. Found: C, 51.78; H, 4.27.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)C_6H_5)^+PF_6^-$ (6). α-Methylstyrene (80 μL, 73 mg, 0.62 mmol) was added to a stirred solution of **1** (273 mg, 0.564 mmol) in CH_2Cl_2 (45 mL) at 0 °C. Evaporation of solvent, extended pumping under high vacuum, and recrystallization from acetone (8 mL) and ether (45 mL) at −78 °C gave solid **6** (200 mg, 59%): ^{1}H NMR (acetone-d_6) δ 12.24 (d, J = 12.5 Hz, μ-CH), 7.6–7.3 (m, 5 H, C_6H_5), 5.75, 5.49 (10 H, C_5H_5), 3.83 (dd, J = 11.5, 9.8 Hz, =CHR), 3.60 (m, CHMePh), 1.65 (d, J = 6.2 Hz, CH_3); ^{13}C{^{1}H} NMR (CD_3NO_2, −8 °C) δ 242.1 (μ-CO), 211.6 (CO), 174.9 (μ-CH), 145.9 (ipso C_6H_5), 130.3, 128.3, 128.1, (C_6H_5), 102.8 (=CHR), 91.4, 91.0 (C_5H_5), 52.3 (CHMePh), 15.6 (CH_3), IR (CH_2Cl_2) 2020 (s), 1998 (w), 1865 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{21}F_6Fe_2O_3P$: C, 45.88; H, 3.52. Found: C, 45.57; H, 3.50.

Similarly, reaction of α-methylstyrene (36 mg, 0.31 mmol) with **1-*d*** (130 mg, 0.27 mmol) in CH_2Cl_2 gave **6-*d*** (100 mg, 62%): ^{2}H{^{1}H} NMR (acetone) δ 12.3.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)C(CH_3)_3)^+PF_6^-$ (7). 2,3,3-Trimethyl-1-butene (100 μL, 71 mg, 0.72 mmol) was added to a stirred solution of **1** (96 mg, 0.198 mmol) in CH_2Cl_2 (30 mL) at −78 °C. The solution was warmed to ambient temperature, solvent was evaporated, and the resulting solid was recrystallized from acetone–ether to give **7** (87 mg, 78%) as a brown-red solid: ^{1}H NMR

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(CD_2Cl_2) δ 11.77 (br d, J = 11.5 Hz, μ-CH), 5.48, 5.21 (10 H, C_5H_5), 3.38 (dd, J = 11.5, 10 Hz, =CH), 1.90 (dq, J = 10, 6.7 Hz, CHMe), 1.14 (s, 9 H, CH_3), 1.04 (d, J = 6.7 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 241.4 (μ-CO), 215.1 (CO), 174.6 (μ-CH), 108.2 (=CHR), 92.7, 89.8 (C_5H_5), 54.9 (CH=*C*HC), 36.1 (CMe_3), 28.3 ($C(CH_3)_3$), 16.7 (CH_3); IR (CH_2Cl_2) 2020 (s), 1995 (w), 1864 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{25}F_6Fe_2O_3P$: C, 43.33; H, 4.33. Found: C, 43.20; H, 4.22.

Similarly, reaction of 2,3,3-trimethyl-1-butene (21 mg, 0.21 mmol) with **1-*d*** (60 mg, 0.12 mmol) in CH_2Cl_2 gave **7-*d*** (55 mg, 76%): $^2H\{^1H\}$ NMR (acetone) δ 12.15.

[(C_5H_5)(CO)Fe]$_2$(μ-CO)[μ-CHCH=C(CH_3)($C(CH_3)_3$)] (8). 2,3,3-Trimethyl-1-butene (100 μL, 0.72 mmol) was added to a stirred suspension of **1** (102 mg, 0.21 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The reaction mixture was stirred at ambient temperature for 35 min and then cooled to −50 °C. Trimethylamine (0.92 atm, 235 mL, 8.9 mmol) was added, and solvent was evaporated at ambient temperature. The resulting solid was purified by column chromatography (alumina, 4:1 hexane/CH_2Cl_2) to give **8** (74 mg, 81%): ^1H NMR (acetone-d_6) δ 12.31 (d, J = 13 Hz, μ-CH), 6.80 (d, J = 13.0 Hz, =CH), 4.86 (s, C_5H_5), 2.14 (s, CH_3), 1.09 (s, $C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) δ 274.5 (μ-CO), 213.2 (CO), 161.8 (d, J = 133 Hz, μ-CHR), 150.0 (d, J = 154 Hz, *C*H=CR_2), 131.7 (CH=*C*R_2), 87.1 (d, J = 178 Hz, C_5H_5), 36.3 (CMe_3), 28.9 (q, J = 126 Hz, $C(CH_3)_3$), 13.3 (q, J = 127 Hz, CH_3); IR (CH_2Cl_2) 1978 (s), 1940 (m), 1777 (m) cm^{-1}; HRMS calcd for $C_{21}H_{24}Fe_2O_3$ 436.0417, found 436.0419.

Similarly, a solution of 2,3,3-trimethyl-1-butene (100 μL, 0.72 mmol) and **1-*d*** (90 mg, 0.186 mmol) was reacted with NMe_3 (1.0 atm, 235 mL, 10 mmol) to give **8-*d*** (73 mg, 90%): $^2H\{^1H\}$ NMR (acetone) δ 12.3.

[(C_5H_5)(CO)Fe]$_2$(μ-CO)(μ-CHCH=C(C_6H_5)$_2$) (9). 1,1-Diphenylethylene (95 μL, 97 mg, 0.54 mmol) was added to a stirred solution of **1** (160 mg, 0.331 mmol) in CH_2Cl_2 (40 mL) at −30 °C. A saturated aqueous solution of $NaHCO_3$ (3 mL) and acetone (10 mL) was added at ambient temperature. The solution was dried ($MgSO_4$), filtered, and evaporated to dryness. The resulting solid was purified by column chromatography (alumina, CH_2Cl_2) and crystallization from CH_2Cl_2–hexane solution to give **9** (80 mg, 46%) as dark red crystals: ^1H NMR (acetone-d_6) δ 11.37 (d, J = 13.4 Hz, μ-CH), 7.7–7.1 (m, 11 H, C_6H_5 and μ-CH=C*H*R), 4.76 (s, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 271.5 (μ-CO), 214.6 (CO), 157.8 (μ-CHR), 143.6, 142.8, 131.5, 129.4, 127.9, 127.1 (C_6H_5 and C=C), 88.7 (C_5H_5); IR (CH_2Cl_2) 1976 (s), 1941 (m), 1782 (m) cm^{-1}; HRMS calcd for $C_{28}H_{22}Fe_2O_3$ 518.0261, found 518.0263.

[(C_5H_5)(CO)Fe]$_2$(μ-CO)[μ-CHCH=C(CH_3)(C_6H_5)] (10-*E* and 10-*Z*). A saturated aqueous solution of $NaHCO_3$ (1.5 mL) was added to a stirred solution of **6** (45 mg, 0.075 mmol) in acetone (10 mL). Solvent was evaporated, and the resulting solid was purified by column chromatography (alumina, Et_2O) to give a 70:30 mixture of **10-E** and **10-Z** (15 mg, 44%): ^1H NMR (acetone-d_6) major isomer, **10-E**, δ 12.18 (d, J = 13.4 Hz, μ-CHR), 7.6–7.2 (m, C_6H_5 and =CHR), 4.95 (s, C_5H_5), 2.50 (s, CH_3); minor isomer, **10-Z**, δ 11.58 (d, J = 13 Hz, μ-CH), 7.6–7.2 (m, C_6H_5), 6.86 (d, J = 13.4 Hz, =CH), 4.70 (s, C_5H_5), 2.09 (s, CH_3); ^{13}C NMR (acetone-d_6) major isomer, **10-E** δ 272.3 (μ-CO), 214.5 (CO), 160.1 (d, J = 137 Hz, μ-CHR), 157.1 (d, J = 155 Hz, =CHR), 145.0 (ipso, C_6H_5), 129.3 (d, J = 157 Hz, C_6H_5), 126.5 (d, J = 155 Hz, C_6H_5), 126.0 (=CMePh), 88.6 (d, J = 175 Hz, C_5H_5), 25.9 (q, J = 121 Hz, CH_3); minor isomer, **10-Z**, δ 157.6 (d, J = 130 Hz, μ-CHR), 155.4 (d, J = 154 Hz, =CHR), 122.0 (=CMePh), 16.2 (q, J = 128 Hz, CH_3); IR (CH_2Cl_2) 1975 (s), 1945 (w), 1777 (m) cm^{-1}; HRMS calcd for $C_{23}H_{20}Fe_2O_3$ 456.0105, found 456.0105.

Similarly, treatment of **6-*d*** (60 mg, 0.10 mmol) with $NaHCO_3$ gave a 70:30 mixture of **10-E-*d*** and **10-Z-*d*** (20 mg, 44%): $^2H\{^1H\}$ NMR (CH_2Cl_2) δ 12.1, 11.6.

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Registry No. 1, 82660-14-8; **1-*d***, 90388-70-8; **2**, 102234-50-4; **2-*d***, 102260-79-7; **3**, 102234-52-6; **4**, 102234-54-8; **4-*d***, 102234-65-1; **5**, 102234-56-0; **6**, 102234-58-2; **6-*d***, 102234-67-3; **7**, 102234-60-6; **7-*d***, 102234-69-5; **8-*E***, 102234-61-7; **8-*E*-*d***, 102234-70-8; **8-*Z***, 102339-55-9; **8-*Z*-*d***, 102339-56-0; **9**, 102234-62-8; **10-*E***, 102234-63-9; **10-*E*-*d***, 102234-71-9; **10-*Z***, 102339-53-7; **10-*Z*-*d***, 102339-54-8; 1-methylcyclohexene, 591-49-1; (2-methyl-1-propenyl)benzene, 768-49-0; *trans*-stilbene, 103-30-0; 1,1-diphenylethylene, 530-48-3; 1,1-di-*p*-tolylethylene, 2919-20-2; α-methylstyrene, 98-83-9; 2,3,3-trimethyl-1-butene, 7439-89-6; Fe, 7439-89-6; D_2, 7782-39-0.

Identification of Some Intermediates in the Titanocene-Catalyzed Dehydrogenative Coupling of Primary Organosilanes

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Abstract: Two new compounds, **2** and **3**, were observed by NMR spectroscopy in $PhSiH_3$ undergoing dehydrogenative polymerization under the catalytic influence of $Cp_2Ti(CH_3)_2$. With use of slightly different reaction conditions, these two compounds were synthesized in good yields and their structures established by NMR spectroscopy and X-ray crystallography. Compound **2** is a dimer of Cp_2TiSiH_2Ph in which dimerization occurs through a pair of Ti–H–Si bridges. Compound **3** has the structure [$Cp_2Ti(\mu\text{-}H)(\mu\text{-}HSiHPh)TiCp_2$]. Under ambient conditions **2** spontaneously decomposes into **3** with production of poly(phenylsilane). **3** is transformed into **2** in the presence of excess $PhSiH_3$. Some chemistry and ESR spectroscopic properties of these two unusual compounds are described, and their possible involvement in the polymerization reaction is discussed.

We have recently reported the dehydrogenative coupling of primary organosilanes to linear polysilanes, under the catalytic influence of dialkyltitanocenes and zirconocenes[2,3] (eq 1). This reaction provides a facile new method for the generation of Si–Si bonds which gives no obnoxious byproducts and furnishes polysilanes of a type not easily accessible by the classical routes of active metal dehalogenation of halosilanes.[4]

$$n\mathrm{RSiH_3} \longrightarrow -(\mathrm{Si}(\mathrm{R})\mathrm{H})_n- + n\mathrm{H_2} \qquad (1)$$

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